Hypervalent Chlorine Nitrates: Implications for Stratospheric Chlorine Chemistry

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It has been known for many years that high levels of chlorine radicals (ClO_x) observed in the polar stratosphere couple with nitrogen oxides (NO_x), resulting in the removal of reactive chlorine species by conversion into temporary reservoir species. Of the various possible reactions between the ClO_x and NO_x families, the association reaction between ClO and NO_2 to produce chlorine nitrate, $ClONO_2$, has been considered the most significant:

$$ClO + NO_2 + M \rightarrow ClONO_2 + M \qquad (1)$$

The suggestion that $ClONO_2$ could be an important reservoir species was first made by Rowland et al. in 1976. Since then, a significant effort has been expended in elucidating the chemistry of $ClONO_2$ in the stratosphere. Also, a large number of field measurements have been made to ascertain the abundance of $ClONO_2$ in the chemically perturbed region of the polar vortex.

Despite the enormous work, there are still discrepancies in balancing the atmospheric chlorine budget. Researchers believe that additional long-time chlorine reservoir species may be involved besides the currently recognized chlorine reservoirs, $ClONO_2$ and hydrogen chloride (HCl). Attempts to improve the current understanding have led to the conclusion that higher oxides of chlorine heretofore overlooked may account for the missing reservoir of inorganic chlorine in the stratosphere. This speculation arose partly from the ground based measurements that detected extraordinarily high concentrations of OClO in the polar vortex, which is believed to be produced primarily by the coupling between ClO and bromine oxide (BrO). In addition, the observation of OClO and NO_3 in the polar stratosphere has strengthened the notion that many more reactions are possible between the NO_x and ClO_x families. In response to these findings, some effort has been directed at the alternative possibility of gas-phase reservoir species resulting from the reactions of OClO with NO_3 and ClO with NO_3.

Friedl et al., in work performed at Jet Propulsion Laboratory (JPL), examined the products of the reaction between OClO and NO_3 from T = 220 to 298 kelvin (K) using a flow reactor and infrared (IR), visible, and ultraviolet (UV) spectroscopic analysis. IR and UV absorption features observed at low temperature (<230 K) were assigned to the novel compound chloryl nitrate, O_2ClONO_2 (fig. 1).

$$OClO + ONO_2 + M \rightarrow O_2ClONO_2 + M \qquad (2)$$

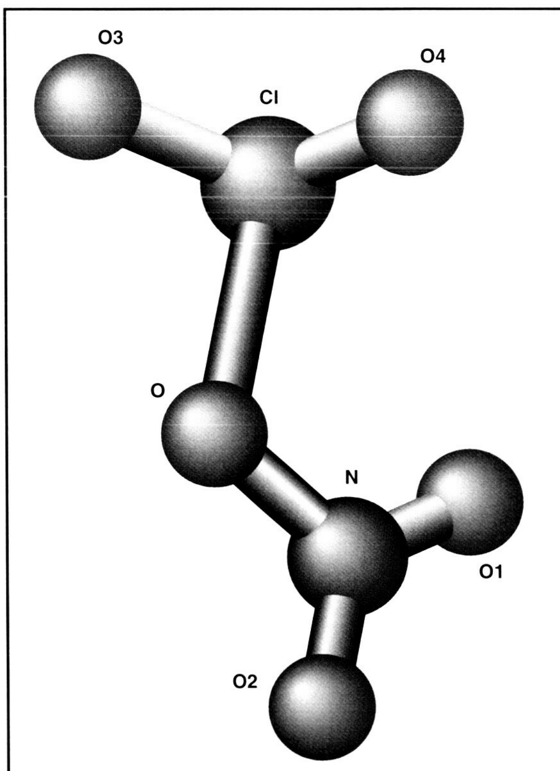

Fig. 1. Novel compound chloryl nitrate, O_2ClONO_2.

Using a one-dimensional model they deduced that chloryl nitrate may exist in significant concentrations in the "collar" region of the polar vortex, where both the reactants are likely to exist in the nighttime air mass. However, in a later study Boyd et al. found no evidence for the occurrence of the homogeneous reaction NO_3 + OClO → products at room temperature, in disagreement with Friedl et al.

In general, the higher oxides of chlorine nitrate could be important if they are produced in sufficient amounts to act as temporary or long-term reservoirs for both odd chlorine and odd nitrogen species. In particular, the possibility that the hypervalent compounds might act as reservoir species is bolstered by previous studies from our laboratory that have shown their electronic spectra to be shifted to higher energy, thereby ensuring their photostability in the stratosphere. Further, independent of their atmospheric significance, the recombination products are interesting molecules from the viewpoint of structural chemistry. Therefore, it is important to establish the properties of these oxides in order to aid in the interpretation of laboratory and atmospheric observations. In the present study, we have considered the following reactions as the possible pathways for adduct formation:

$$ClO + ONO_2 + M \rightarrow ClOONO_2 + M \quad (4)$$

$$ClOO + NO_2 + M \rightarrow ClOONO_2 + M \quad (5)$$

$$OClO + NO_2 + M \rightarrow OClONO_2 + M \quad (6)$$

$$OClO + NO_2 + M \rightarrow O_2ClNO_2 + M \quad (7)$$

$$ClOO + ONO_2 + M \rightarrow ClOOONO_2 + M \quad (8)$$

$$OClO + ONO_2 + M \rightarrow OClOONO_2 + M \quad (9)$$

$$OClO + ONO_2 + M \rightarrow O_2ClONO_2 + M \quad (10)$$

Using the tools of computational quantum chemistry, we have established that the $OClONO_2$, O_2ClNO_2, and $OClOONO_2$ compounds are thermodynamically not very stable, if at all, and will, therefore, play no role in stratospheric chlorine chemistry. On the other hand, the $ClOONO_2$, $ClOOONO_2$, and O_2ClONO_2 compounds are thermodynamically stable enough that they could exist in certain regions of the stratosphere. Their weakest bond energy is computed to be about 7 kcal/mol, indicating that in the upper stratosphere (where it is hotter), these compounds are more likely to dissociate. By comparing our computed IR spectra for O_2ClONO_2 with the experimentally observed one from Friedl et al., we have also shown conclusively that they did indeed observe O_2ClONO_2 from the reaction of OClO + NO_3, contrary to the conclusions of Boyd et al. In fact, our thermodynamic analysis of the stability of O_2ClONO_2 is consistent with both the experiments from Friedl et al. and Boyd et al. since the latter were performed at room temperature (298 K) while the former extended down to 220 K.

Other important physical characterization data for the $ClOONO_2$, $ClOOONO_2$, and O_2ClONO_2 compounds also have been provided, including equilibrium structures, dipole moments, full IR spectra, heats of formation, and bond energies for possible dissociation pathways, in order to aid future experimental, modeling, and field measurement studies involving these compounds. Finally, our computational studies have further established the importance of hypervalent halogen compounds in stratospheric chemistry.

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